A Novel Design of Fixed-bed Column Using a High Gradient Magnetic Field

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A new magnetically assisted wastewater treating system has been suggested for Cr^{VI}-contaminated waters using a novel and strong Cr-sorbent, namely, schwertmannite. The system contains a fixed-bed column, put in a high magnetic field, which was alternately packed with schwertmannite fine particles and iron wools as a ferromagnetic porous media. The obtained results confirm its high efficiency.

Widespread usage of chromium in a variety of industrial applications has encouraged an accelerating progress in environmental researches to control Cr ion concentration in industrial discharging waters. Iron oxides (hydroxides) have gained a lot of interest to be used as novel and strong chemical adsorbents and catalyst during the last decade because of their abundance and unique surface catalytic properties as well as the new developments on their synthesis especially in nanosize scales which denote some unique physical and chemical properties to them.¹ In our pervious studies, we have illustrated that schwertmannite as an iron oxyhydroxide material with the ideal formula of Fe₈O₈(OH)₆SO₄ has a quite high adsorption capacity of phosphate and fluoride ions with a high regeneration capability in a simple method. Its extremely fine particle size, however, makes it difficult to be applied along with the classical filtration techniques for solid-liquid separation. Thus, magnetic filtration can be considered as a suitable candidate for separation of fine schwertmannite particles from its suspended liquid.² Magnetic filtration, however, has some inherent limitations to be utilized as a continuous filtering system because of time-dependent plugging of its matrix.

The most optimal configuration for continuous-flow adsorption is the packed-bed column which gets gradually saturated from the feed to the solution exit end. High-quality fixed-bed column hardware is the subject of several U.S. patents. In our study work, the experimental trials of the process have been conducted for many times by directly packing the column with the fine-particle-sized schwertmannite, as one of the most strong Cr adsorbents. Extremely fine particles and mud-like properties of the adsorbent, however, has caused a variety of problems to the system such as high-pressure drop, mass-transfer resistance, and so on. To solve the problems dealing with the system, a magnetic-fixed-bed column, as a novel designation of the fixed-bed columns, has been presented in this study. Moreover, the batch Cr^{VI} adsorption data containing equilibrium model to predict the adsorption characteristics of the adsorbent has been given.

All chemicals used were of high purity and analytical grades. The schwertmannite powder as the chemical adsorbent of Cr^{VI} in these experiments was made by homogenous hydrol-

ysis of iron(III) salt (Fe₂(SO₄)₃•*n*H₂O) according to the methods mentioned in our pervious works.^{2,3} Stock solution of 130-mg/L Cr^{VI} for use in the fixed column experiment was prepared by dissolving of a known amount of K₂Cr₂O₇ in dionized water. In the batch mode adsorption trials, 50 mL of the solution with desired concentrations of Cr and the adsorbent were mixed in a 100-mL bottle and shaken for about 5 h to reach to the equilibrium state. Then the yielded solution was filtered through a paper filter, and then chromium concentration in the filtrate was analyzed to assess the adsorption behavior of Cr^{VI} on the adsorbent. Diluted HCl and NaCl were used to adjust the pH values of the solution samples containing Cr ions and schwertmannite.

Cr concentration was measured by using an inductively coupled plasma atomic emission spectroscopy (ICP). The particle size distribution and the mean size of the schwertmannite particles were determined using a laser-scattering particle size distribution analyzer (LA-920). The specific surface area of schwertmannite particles was measured using BET analysis.

Adsorption isotherm study was conducted at pH 4.2 and is presented in the form of equilibrium uptake against equilibrium concentration. Equilibrium data is important in evaluating the adsorption capacity of an adsorbent for a given adsorbate. In this section, Cr^{VI} adsorption results at pH 4.2 are presented in the form of equilibrium isotherms. If at pH 4.2, the effective active sites are assumed to consist of neutral sites (pH_{pzc} of schwertmannite: ≈ 4.2),² which are distributed uniformly, then it is justifiable to describe the equilibrium data with the Langmuir isotherm. The equilibrium data of Cr^{VI} adsorption on to schwertmannite was fitted to the linearized Langmuir isotherm as written below;

$$q_{\rm e} = \frac{q_{\rm m} b C_{\rm e}}{1 + b C_{\rm e}} \tag{1}$$

where q_e is equilibrium uptake, q_m is Langmuir maximum capacity, C_e is equilibrium concentration (mg F/L), and *b* is affinity coefficient. The maximum capacity, q_m , and the affinity coefficient, *b*, were obtained as 178.6 mg/g and 0.0042 L/mg, respectively. From several other data published in the literature, it is observed that the capacity of schwertmannite for Cr^{VI} is competitively higher than those of other sorbents.

Fixed-bed column is the most commonly used method in industrial application of chemical adsorbents wherein convection along the column axial direction and axial dispersion are the mass transport mechanisms in the bulk phase. The schwertmannite with the measured particle size ranged from 0.3 to several microns and the specific surface area of $165 \text{ m}^2/\text{g}$ have a specific colloidal property which remarkably increases flow-transfer resistance through the bed, in its directly application to a fixed-



Figure 1. A schematic view of the magnetic fixed-bed column.

bed system, owing to its mud-like characteristic. To overcome these limitations associated with the process and avoid clogging the column, the application of multilayer packed bed is inevitable. A novel-packed column type firstly introduced here is named "magnetic-fixed-bed column" which jointly works with a high gradient magnetic field to improve the main characters of the fixed columns.

In this designation, ferromagnetic wools or wires as high porous media are alternately inserted into the column which is loaded by the adsorbent of roughly the same height as wools. Figure 1 exhibits a small-scale physical model of the suggested process wherein schwertmannite powder was packed in a glassmade column with 2-cm diameter in a manner that ferromagnetic wool layers were alternately laid among the adsorbent layers. In each layer of the adsorbent and porous media, 1 g of schwertmannite and 0.4 g of iron wools were packed, respectively. The overall height of the bed depth was 5 cm. After fixing the column, it was located in the place of the highest gradient of a magnetic field with 4T of magnetic intensity. The prepared stock solution containing CrVI was then passed through the fixed-bed column located in the high magnetic field in an upward model using a peristaltic pump. The effluent samples were collected at certain time intervals and analyzed for Cr concentration

The imposed high magnetic field in this process has a great role to retain the shape and the fitness of the column bed during the feeding of the bed. In fact, the magnetization force acts as a holding force to maintain the bed's condition to be constant. That is, as a result of the strongly keeping the ferromagnetic wires to the column's wall by the magnetization force without requiring to any foreign forces, we have the advantage in the hardware of the fixed-bed compared to the usual fixed-beds. Figure 2 represents the concentration time variation of the mag-



Figure 2. Concentration time variation of the magnetic-fixedbed column.

netic-fixed-bed as an assessment of the process wherein C_0 and C are the Cr concentrations in the influent and effluent, respectively. According to the obtained results, the concentration time variation in the process is thoroughly similar to the typical curves of a fixed-bed column,⁴ which confirms the successful operation of this process. For 4 g of the used schwertmannite, the total amount of the Cr ion adsorbed was computed, from the data obtained from Figure 2, as 740 mg which is equal to 185 mg Cr/g of the schwertmannite. That is, Cr-adsorption in this process was increased compared to the maximal Cr adsorption trials.

The invariable amounts of the output slurries in each interval indicate that the physical condition of the column bed was unchanged during the process. In addition, the contact time between the loaded slurry and the adsorbent may be increased as a consequence of the magnetic field effect on the flow pattern of the fed slurry through the bed which may result in an increase on the ion adsorption in the process.

In this study, magnetic-fixed-bed column has been introduced as a novel design of a fixed-bed column which is loaded by alternately schwertmannite, as an adsorbent, and ferromagnetic wools, as a high porous media, working under high magnetic field as a very efficient media for Cr^{VI} removal from water. Application of a magnetization force in this process not only introduces the advantage in the experimental set-up of the fixed-bed but also keeps the bed's condition constant as significant parameters for bed columns dealing with submicron and nanoparticle adsorbents.

This work was partially supported by JSPS Asian Core Program "Construction of the World Center on Electromagnetic Processing of Materials."

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